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(54) CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a curable composition giving a cured material which ensures practical curability and recovery properties and has mechanical properties including high strength and high elongation.

SOLUTION: The curable composition comprises (A) an organic polymer having at least one silicon-containing group which has a hydroxy group or a hydrolyzable group bonded to the silicon atom and which is crosslinkable by forming siloxane bonds, and (B) one or more sorts of metal carboxylates selected from calcium carboxylate, vanadium carboxylate, iron carboxylate, titanium carboxylate, potassium carboxylate, barium carboxylate, manganese carboxylate, nickel carboxylate, cobalt carboxylate and zirconium carboxylate.

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. *** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim 6]

[Claim 1]

(A) While containing an organic polymer and (B) carboxylic acid zirconium which have a hydroxyl group or a hydroxylate but combined with a silicon atom, and have at least one silicon content group as an essential ingredient, a (C) ingredient.

(B) A hardenability constituent, wherein a carboxylic acid zirconium of an ingredient is a carboxylic acid zirconium in which the melting point has an acid radical of carboxylic acid which is 65 ° or less.

[Claim 2]

(A) A number average molecular weight is within the limits of 500-50,000, and an organic polymer of an ingredient is a general formula to an end and/or a side chain of a main chain (1):

[Formula 1]



(R¹ and R² among a formula) They are an alkyl group of the carbon numbers 1-20, an aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20, or (R¹)₂SiO independently, respectively. (R³) respectively — independent — the substitution of the carbon numbers 1-20, or an unsubstituted hydrocarbon group — it is — it is the Tof ORGANO alloy group shown. X is a hydroxyl group or a hydroxyloxy basis independently, respectively, a is 0, 1, 2, or 3, b is 0, 1, or 2, and a and b are not simultaneously set to 0, m — the integer of 0, or 1-19 — it is — the hardenability constituent according to claim 1 having one or more hydrolytic silyl groups per molecule expressed.

[Claim 3]

The hardenability constituent according to claim 2, wherein X is an alkoxy group.

[Claim 4]

(A) A hardenability constituent given in any 1 paragraph of Claims 1-3 whose organic polymers of an ingredient are a polyalkylene series polymer and/or a saturated hydrocarbon system polymer.

[Claim 5]

The hardenability constituent according to claim 4 which is a polymer, wherein said saturated hydrocarbon system polymer has a repeating unit resulting from isobutylene 50% of the weight or more in a total amount.

[Claim 6]

(B) A hardenability constituent given in any 1 paragraph of Claims 1-5 to which a carboxylic acid zirconium of an ingredient uses as the main ingredients carboxylic acid metal salt expressed with a general formula (12):

Zr(O)(OOCR)₂ (12)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a silicon-carbon double bond.)

[Claim 7]

(B) The hardenability constituent according to any one of claims 1 to 8 which is the carboxylic acid metal salt which has an acid radical of carboxylic acid whose carbon numbers in which carboxylic acid metal salt of an ingredient contains carbon of a carbonyl group are 2-17.

[Claim 8]

(B) A hardenability constituent given in any 1 paragraph of Claims 1-8 which are metal salt of a carboxylic acid group content compound in which carboxylic acid metal salt of an ingredient is chosen from acetic acid, 2-ethylacetic acid, neo decanoic acid, oleic acid, or naphthenic acid.

[Claim 9]

(A) A hardenability constituent given in any 1 paragraph of Claims 1-8 containing the (B) ingredient of quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the quantity to ingredient 100 weight section.

[Claim 10]

(A) A hardenability constituent given in any 1 paragraph of Claims 1-8 containing the (B) ingredient of quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the (B) ingredient, the (C) ingredient 0.01 - 20 weight sections to ingredient 100 weight section.

[Translation done.]

zirconium.

[0013] An amine compound is related with the aforementioned hardenability constituent which becomes as an essential ingredient as a (C) ingredient.

[0014] As a desirable embodiment, a number average molecular weight is within the limits of 500-50,000, and an organic polymer of the (A) ingredient is a general formula to an end and/or a side chain of a main chain (1):



[Formula 1]

[0015] (R¹ and R² among a formula) They are an alkyl group of the carbon numbers 1-20, an aryl group of the carbon numbers 6-20, an allyl group of the carbon numbers 7-20 or (R³)₃SiO independently, respectively. - (R) respectively - independent - the substitution of the carbon numbers 1-20, or an unsaturated hydrocarbon group - it is - it is the Tert ORGANO siloxy group atom. - a hydroxyl group or a hydroxyloxy salt independently, respectively, 1, 2, or 3 is 1, 2, or 3, and 2 and 3 is not simultaneously set to 0. The integer of n is 1 or 19. i.e., it is linked with a hardenability constituent given in said either having one or more hydroxyloxy silyl groups per molecule and/or.

[0016] It is related with the aforementioned hardenability constituent characterized by X being an alkoxy group as a desirable embodiment.

[0018] As a desirable embodiment, the organic polymer of the (A) ingredient is related with a hardenability constituent given in said either which is a polyoxyalkylene series polymer and/or a saturated hydrocarbon system polymer.

[0019] As a desirable embodiment, said saturated hydrocarbon system polymer is related with the aforementioned hardenability constituent which is a polymer having a repeating unit resulting from isobutylene 50% of the weight or more in a total amount.

[0020] As a desirable embodiment, a carboxylic acid zirconium of the (B) ingredient is related with a hardenability constituent given in said either which uses as the main ingredients carboxylic acid metal salt expressed with a general formula (12).

(12) (OCOR)₂ (12)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.)

As a desirable embodiment, carboxylic acid metal salt of the (B) ingredient is related with a hardenability constituent given in said either which is the carboxylic acid metal salt in which the melting point has an acid radical of carboxylic acid which is 65 ° or less.

As a desirable embodiment, a carbon number in which carboxylic acid metal salt of the (B) ingredient contains a carboxyl group is related with a hardenability constituent given in said either which is a carbon number in which the carboxylic acid metal salt which has an acid radical of carboxylic acid which is 2-17.

As a desirable embodiment, carboxylic acid metal salt of the (B) ingredient is related with a hardenability constituent given in said either which is metal salt of a carboxylic acid group content compound chosen from octyloic acid, 2-ethylhexanoic acid, n-octanoic acid, oleic acid, or

naphthenic acid.

[0023] It is related with a hardenability constituent given in said either containing the (B) ingredient of a quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the (B) ingredient to (A) ingredient 100 weight section as a desirable embodiment.

[0024] It is related with a hardenability constituent given in said either containing the (B) ingredient of a quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the (B) ingredient, the (C) ingredient 0.01 - 20 weight sections to (A) ingredient 100 weight section as a desirable embodiment.

[0025] The mode of Carrying Out the Invention

Hereafter, this invention is explained in detail.

[0026] Restriction in particular does not have a principal chain skeleton of an organic polymer which has a reactive silicon group used for the invention, and it can use a thing with various kinds of principal chain skeletons.

[0027] Specifically, A polyoxyethylene, polyoxypropylene, polyoxy butylene, Polyoxy tetramethylene, a polyoxyethylene polyoxypropylene copolymer, Or polyoxyalkylene series polymers, such as a polyoxyethylene polyoxypropylene, polyoxybutylene, An ethylene-propylene system copolymer. The copolymer of polyisobutylene, isobutylene, isoprene, etc., polyisoprene. A copolymer with polyisoprene, isoprene or butadiene, acrylonitrile, styrene, etc. Hydrocarbon system polymers, such as polyethylene, polyolefin, polyethylene system polymer produced by hydrogenating polyolefins or these as a hydrocarbon system polymer. Condensation with dibasic acid, such as adipic acid, and glycol. Or the polyester system polymer obtained by the ring opening polymerization of lactone: The polyuretic ester produced by carrying out the radical polymerization of the monomers, such as ethyl acrylate and butyl acrylate, Vinyl-based polymers, such as an acrylic ester system copolymer with acrylic ester, such as ethyl acrylate and butyl acrylate, vinyl acetate, acrylonitrile, methyl methacrylate, styrene, etc. A vinyl polymer. Nylon 610 by the condensation polymerization of the nylon 6 by the ring opening polymerization of epsilon caprolactam, hexamethylenediamine, Nylon 66 by the condensation polymerization of adipic acid and hexamethylenediamine, and abasic acid. Nylon 11 by the condensation polymerization of epsilon-aminoundecanoic acid. Condensation polymerization is carried out from polyamide system polymer, for example, bisphenol A, and the carbonyl chlorides which have a two or more-ingredient ingredient among Nylon 12 by the ring opening polymerization of epsilon-amine RAURO lactam, and the above-mentioned nylon, such as copolyamide. The polycarbonate system polymer manufactured, a diallyl phthalate system polymer etc., are illustrated.

[0028] Since acquisition and manufacture are easy among polymers with the above-mentioned principal chain skeleton, a polyoxyalkylene series polymer, a hydrocarbon system polymer, a polyester system polymer, a vinyl system copolymer, a polycarbonate system polymer, etc. are preferred. A saturated hydrocarbon system copolymer, and a polyoxyalkylene series polymer and a vinyl system copolymer have a comparatively low glass transition temperature, and their hardened material obtained is especially preferred from excellent in cold resistance.

[0029] As a saturated hydrocarbon system polymer which has a reactive silicon group used for this invention, the reactive silicon group content saturated hydrocarbon system polymer obtained from saturated hydrocarbon system polymers, such as polyisobutylene, hydrogenated polybutadiene, and polyisoprene polyisopren, is related.

[0030] The reactive silicon group contained in the organic polymer which has a reactive silicon group is a basis which can construct a bridge by formation of the siloxane bond which is a reaction which has the hydroxyl group or hydroxyloxy basis combined with the silicon atom, and is accelerated with the carboxylic acid metal salt which is the (B) ingredient.

3 paint roll according to the formula shown in Table 2, using the reactive silicon group content polyoxysilylene series polymer (A-1) obtained in the synthetic example 1, and was considered as base resin.

[0166]

Next, as a (B) ingredient which is a silyl condensation catalyst, lauryl amine was further measured for the various carboxylic acid metal salt shown in Table 1 to the above-mentioned base resin as a (C) ingredient, the spatula was used for it, and it stirred and mixed for 3 minutes. It was made for all the numbers of mole of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become the same here.

[0167]

The mold, about 3 mm thick and filled up with the spatula after mixing, and care of health on 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 510, 520, 530, 540, 550, 560, 570, 580, 590, 600, 610, 620, 630, 640, 650, 660, 670, 680, 690, 700, 710, 720, 730, 740, 750, 760, 770, 780, 790, 800, 810, 820, 830, 840, 850, 860, 870, 880, 890, 900, 910, 920, 930, 940, 950, 960, 970, 980, 990, 1000, 1010, 1020, 1030, 1040, 1050, 1060, 1070, 1080, 1090, 1100, 1110, 1120, 1130, 1140, 1150, 1160, 1170, 1180, 1190, 1200, 1210, 1220, 1230, 1240, 1250, 1260, 1270, 1280, 1290, 1300, 1310, 1320, 1330, 1340, 1350, 1360, 1370, 1380, 1390, 1400, 1410, 1420, 1430, 1440, 1450, 1460, 1470, 1480, 1490, 1500, 1510, 1520, 1530, 1540, 1550, 1560, 1570, 1580, 1590, 1600, 1610, 1620, 1630, 1640, 1650, 1660, 1670, 1680, 1690, 1700, 1710, 1720, 1730, 1740, 1750, 1760, 1770, 1780, 1790, 1800, 1810, 1820, 1830, 1840, 1850, 1860, 1870, 1880, 1890, 1900, 1910, 1920, 1930, 1940, 1950, 1960, 1970, 1980, 1990, 2000, 2010, 2020, 2030, 2040, 2050, 2060, 2070, 2080, 2090, 2100, 2110, 2120, 2130, 2140, 2150, 2160, 2170, 2180, 2190, 2200, 2210, 2220, 2230, 2240, 2250, 2260, 2270, 2280, 2290, 2300, 2310, 2320, 2330, 2340, 2350, 2360, 2370, 2380, 2390, 2400, 2410, 2420, 2430, 2440, 2450, 2460, 2470, 2480, 2490, 2500, 2510, 2520, 2530, 2540, 2550, 2560, 2570, 2580, 2590, 2600, 2610, 2620, 2630, 2640, 2650, 2660, 2670, 2680, 2690, 2700, 2710, 2720, 2730, 2740, 2750, 2760, 2770, 2780, 2790, 2800, 2810, 2820, 2830, 2840, 2850, 2860, 2870, 2880, 2890, 2900, 2910, 2920, 2930, 2940, 2950, 2960, 2970, 2980, 2990, 3000, 3010, 3020, 3030, 3040, 3050, 3060, 3070, 3080, 3090, 3100, 3110, 3120, 3130, 3140, 3150, 3160, 3170, 3180, 3190, 3200, 3210, 3220, 3230, 3240, 3250, 3260, 3270, 3280, 3290, 3300, 3310, 3320, 3330, 3340, 3350, 3360, 3370, 3380, 3390, 3400, 3410, 3420, 3430, 3440, 3450, 3460, 3470, 3480, 3490, 3500, 3510, 3520, 3530, 3540, 3550, 3560, 3570, 3580, 3590, 3600, 3610, 3620, 3630, 3640, 3650, 3660, 3670, 3680, 3690, 3700, 3710, 3720, 3730, 3740, 3750, 3760, 3770, 3780, 3790, 3800, 3810, 3820, 3830, 3840, 3850, 3860, 3870, 3880, 3890, 3900, 3910, 3920, 3930, 3940, 3950, 3960, 3970, 3980, 3990, 4000, 4010, 4020, 4030, 4040, 4050, 4060, 4070, 4080, 4090, 4100, 4110, 4120, 4130, 4140, 4150, 4160, 4170, 4180, 4190, 4200, 4210, 4220, 4230, 4240, 4250, 4260, 4270, 4280, 4290, 4300, 4310, 4320, 4330, 4340, 4350, 4360, 4370, 4380, 4390, 4400, 4410, 4420, 4430, 4440, 4450, 4460, 4470, 4480, 4490, 4500, 4510, 4520, 4530, 4540, 4550, 4560, 4570, 4580, 4590, 4600, 4610, 4620, 4630, 4640, 4650, 4660, 4670, 4680, 4690, 4700, 4710, 4720, 4730, 4740, 4750, 4760, 4770, 4780, 4790, 4800, 4810, 4820, 4830, 4840, 4850, 4860, 4870, 4880, 4890, 4900, 4910, 4920, 4930, 4940, 4950, 4960, 4970, 4980, 4990, 5000, 5010, 5020, 5030, 5040, 5050, 5060, 5070, 5080, 5090, 5100, 5110, 5120, 5130, 5140, 5150, 5160, 5170, 5180, 5190, 5200, 5210, 5220, 5230, 5240, 5250, 5260, 5270, 5280, 5290, 5300, 5310, 5320, 5330, 5340, 5350, 5360, 5370, 5380, 5390, 5400, 5410, 5420, 5430, 5440, 5450, 5460, 5470, 5480, 5490, 5500, 5510, 5520, 5530, 5540, 5550, 5560, 5570, 5580, 5590, 5600, 5610, 5620, 5630, 5640, 5650, 5660, 5670, 5680, 5690, 5700, 5710, 5720, 5730, 5740, 5750, 5760, 5770, 5780, 5790, 5800, 5810, 5820, 5830, 5840, 5850, 5860, 5870, 5880, 5890, 5900, 5910, 5920, 5930, 5940, 5950, 5960, 5970, 5980, 5990, 6000, 6010, 6020, 6030, 6040, 6050, 6060, 6070, 6080, 6090, 6100, 6110, 6120, 6130, 6140, 6150, 6160, 6170, 6180, 6190, 6200, 6210, 6220, 6230, 6240, 6250, 6260, 6270, 6280, 6290, 6300, 6310, 6320, 6330, 6340, 6350, 6360, 6370, 6380, 6390, 6400, 6410, 6420, 6430, 6440, 6450, 6460, 6470, 6480, 6490, 6500, 6510, 6520, 6530, 6540, 6550, 6560, 6570, 6580, 6590, 6600, 6610, 6620, 6630, 6640, 6650, 6660, 6670, 6680, 6690, 6700, 6710, 6720, 6730, 6740, 6750, 6760, 6770, 6780, 6790, 6800, 6810, 6820, 6830, 6840, 6850, 6860, 6870, 6880, 6890, 6900, 6910, 6920, 6930, 6940, 6950, 6960, 6970, 6980, 6990, 7000, 7010, 7020, 7030, 7040, 7050, 7060, 7070, 7080, 7090, 7100, 7110, 7120, 7130, 7140, 7150, 7160, 7170, 7180, 7190, 7200, 7210, 7220, 7230, 7240, 7250, 7260, 7270, 7280, 7290, 7300, 7310, 7320, 7330, 7340, 7350, 7360, 7370, 7380, 7390, 7400, 7410, 7420, 7430, 7440, 7450, 7460, 7470, 7480, 7490, 7500, 7510, 7520, 7530, 7540, 7550, 7560, 7570, 7580, 7590, 7600, 7610, 7620, 7630, 7640, 7650, 7660, 7670, 7680, 7690, 7700, 7710, 7720, 7730, 7740, 7750, 7760, 7770, 7780, 7790, 7800, 7810, 7820, 7830, 7840, 7850, 7860, 7870, 7880, 7890, 7900, 7910, 7920, 7930, 7940, 7950, 7960, 7970, 7980, 7990, 8000, 8010, 8020, 8030, 8040, 8050, 8060, 8070, 8080, 8090, 8100, 8110, 8120, 8130, 8140, 8150, 8160, 8170, 8180, 8190, 8200, 8210, 8220, 8230, 8240, 8250, 8260, 8270, 8280, 8290, 8300, 8310, 8320, 8330, 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14290, 14300, 14310, 14320, 14330, 14340, 14350, 14360, 14370, 14380, 14390, 14400, 14410, 14420, 14430, 14440, 14450, 14460, 14470, 14480, 14490, 14500, 14510, 14520, 14530, 14540, 14550, 14560, 14570, 14580, 14590, 14600, 14610, 14620, 14630, 14640, 14650, 14660, 14670, 14680, 14690, 14700, 14710, 14720, 14730, 14740, 14750, 14760, 14770, 14780, 14790, 14800, 14810, 14820, 14830, 14840, 14850, 14860, 14870, 14880, 14890, 14900, 14910, 14920, 14930, 14940, 14950, 14960, 14970, 14980, 14990, 15000, 15010, 15020, 15030, 15040, 15050, 15060, 15070, 15080, 15090, 15100, 15110, 15120, 15130, 15140, 15150, 15160, 15170, 15180, 15190, 15200, 15210, 15220, 15230, 15240, 15250, 15260, 15270, 15280, 15290, 15300, 15310, 15320, 15330, 15340, 15350, 15360, 15370, 15380, 15390, 15400, 15410, 15420, 15430, 15440, 15450, 15460, 15470, 15480, 15490, 15500, 15510, 15520, 15530, 15540, 15550, 15560, 15570, 15580, 15590, 15600, 15610, 15620, 15630, 15640, 15650, 15660, 15670, 15680, 15690, 15700, 15710, 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17150, 17160, 17170, 17180, 17190, 17200, 17210, 17220, 17230, 17240, 17250, 17260, 17270, 17280, 17290, 17300, 17310, 17320, 17330, 17340, 17350, 17360, 17370, 17380, 17390, 17400, 17410, 17420, 17430, 17440, 17450, 17460, 17470, 17480, 17490, 17500, 17510, 17520, 17530, 17540, 17550, 17560, 17570, 17580, 17590, 17600, 17610, 17620, 17630, 17640, 17650, 17660, 17670, 17680, 17690, 17700, 17710, 17720, 17730, 17740, 17750, 17760, 17770, 17780, 17790, 17800, 17810, 17820, 17830, 17840, 17850, 17860, 17870, 17880, 17890, 17900, 17910, 17920, 17930, 17940, 17950, 17960, 17970, 17980, 17990, 18000, 18010, 18020, 18030, 18040, 18050, 18060, 18070, 18080, 18090, 18100, 18110, 18120, 18130, 18140, 18150, 18160, 18170, 18180, 18190, 18200, 18210, 18220, 18230, 18240, 18250, 18260, 18270, 18280, 18290, 18300, 18310, 18320, 18330, 18340, 18350, 18360, 18370, 18380, 18390, 18400, 18410, 18420, 18430, 18440, 18450, 18460, 18470, 18480, 18490, 18500, 18510, 18520, 18530, 18540, 18550, 18560, 18570, 18580, 18590, 18600, 18610, 18620, 18630, 18640

Table 3, the value of Tb (breaking strength) and Eb (elongation after fracture) of hardened material physical properties is larger.
High elongation and high intensity were shown.

[0173]

(Working example 16-23, comparative example 4)

(A) Using the mixture (A-2) of the isobutylene system polymer and plasticizer which have as an ingredient the reactive silicon group obtained in the synthetic example 2, various additive agents were measured, respectively, and it often kneaded with a 3 paint roll according to the formula shown in Table 4, and was considered as base resin.

[0174]

Next, the various carboxylic acid metal salt shown in Table 4 as a (B) ingredient which is a silanol condensation catalyst was measured, and also as a (C) ingredient which is a curing agent was used together the above-mentioned (A) resin. The result of the measurement is shown in Table 4. In working example 16-28 and the comparative example 16-29, the hardened state was evaluated for 3 minutes to it. It was recuperated at 23 °C for 5 days, and the surface hardened state was evaluated five days afterward. It was made for all the numbers of nols of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become the same here.

[0175]

The evaluation result of the hardened state five days after the combination presentation of base resin, a curing catalyst, etc. is shown in Table 4. What the surface had hardened O in front for five days afterward is shown, and it is shown that x had not hardened five days after.

[0176]

[Table 4]

成分名		硬化剤 (B)										硬化剤 (C)		硬化剤 (D)	
成分名		硬化剤 (B)										硬化剤 (C)		硬化剤 (D)	
成分名		硬化剤 (B)										硬化剤 (C)		硬化剤 (D)	
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